INVESTIGATION OF OBSERVED CHANGES IN TREATED HEMP HURDS

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Abstract

The effort to achieve sustainable development using renewable materials instead of limited ones is the current trend in the construction industry. Need for the development of environmentally friendly products is related to industrial interest in using natural plant fibres as reinforcement in composites. The combination of organic filler and inorganic matrix creates high-quality products such as fibre boards and composites. Industrial hemp fibres are one of the mostly used natural fibres and due to their unique mechanical, thermal insulation, acoustic and antiseptic properties have a great potential in composite materials. However, improving the interfacial bond between fibre and matrix is an important factor in fibre-reinforced composites. Optimizing the adhesion between fibre and inorganic matrix is related to surface treatment processes. This paper deals with morphology characterization, study changes in the chemical composition and structure of hemp fibres using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) before and after physico-chemical treatment.

Key words: Hemp hurds, FTIR spectroscopy, SEM microscopy, treatment process.

1 INTRODUCTION

Natural fibres as alternatives to conventional reinforcements in composite materials are studied for several years. The use of building materials made from renewable resources is particularly interesting for the construction industry. This represents a large opportunity in the field of vegetable fibres that is cost-effective and environmentally friendly. Therefore, to promote the use of composite materials reinforced with vegetable natural fibres could be a way to achieve sustainable and more eco-efficient construction [1].

Traditional building materials are increasingly being replaced by advanced building materials in accordance with sustainable development requirements. Fibre reinforced polymers and fibre reinforced cement represent a group of new composites with advantageous properties [2]. In the scientific sphere as well as in the industrial production, the use of natural lignocellulosic fibres (such as sisal, jute, hemp, bamboo, kenaf, coconut, coir, etc.) as a replacement for synthetic fibres into lightweight composites has received attention in recent years [3]. Vegetable fibres exhibit a set of important advantages, such as wide availability at relatively low cost, biorenewability, ability to be recycled, biodegradability, non-hazardous nature, zero carbon footprint, and interesting physical and mechanical properties [4, 5]. Vegetable fibres can be found in a wide variety of morphologies – diameter, aspect ratio, length, and surface roughness – and form – mainly strands, pulp or staple. Moreover, their surface can be easily modified in order to have a more hydrophilic or hydrophobic character or to attach functional groups [6].

Lignocellulosic biomass has become a promising alternative source of materials for industrial applications. Natural fibres are mainly composed of hemicelluloses, lignin and pectin, moreover, the composition can more or less change according to the growing conditions, the location and the age of the plant [7].

Building materials based on natural lignocellulosic fibres with an inorganic binder represent a group of lightweight materials providing healthy living in buildings [8]. However, their incorporation in a polymer or a mineral matrix involves interface incompatibility between the fibres and the matrix which may be overcome with fibres pre-treatments [9].

The hemp plant, which is a material that is rapidly renewable, carbon-negative, cost-effective, and non-toxic, is one of the most frequently used natural vegetable sources of lignocellulosic fibres in the construction industry is [6]. Technical hemp (Cannabis Sativa L.) is a source of two types of fibres; bast fibres and woody fibres called hurds. The properties of hemp fibres depend on the fibre chemical composition. The bast fibres contain more amounts of cellulose compared to the hemp hurds. Contrary, the contents of hemicelluloses and lignin as amorphous substances are higher in hurds [10]. The nature of plant fibres is determined by their chemical composition. In general, celluloses in natural fibres are identified as a main structural component of the fibre, which is present mainly in crystalline phase. The other components of plant fibres involve hemicelluloses, lignin, and pectin. Hemicelluloses and lignin are present mostly in amorphous phase, which play an important

role in controlling its properties. One of the key problems of plant fibres successful application consists in heterogeneity and hydrophility resulting in the high moisture sorption sensitivity of biomaterial. Hydroxyl groups in structure of cellulose, hemicelluloses, and lignin are responsible for the hydrophility of the plant material [11]. To decrease the hydrophility and modify the cellulosic composition of hemp fibres, physical and physico-chemical treatment processes of material surface are applied in this work.

For the fibres, carbohydrate degradation, Fourier transforms infrared spectroscopy (FTIR) as one of the most effective and important analytical techniques for fibrous material study is used [12, 13]. The FTIR spectroscopy provides the information about molecular fragments, the presence or absence of specific functional groups. The morphology of the natural fibres was evaluated by means of scanning electron microscope analysis (SEM).

This study reports changes in the chemical composition, morphological features, and the structure of hemp hurds after the physical and physico-chemical treatments in comparison to the reference sample using the Fourier transform infrared spectroscopy (FTIR) and the scanning electron microscopy (SEM).

2 EXPERIMENTAL PART

The technical hemp hurds (Figure 1) originating from the Netherlands Company Hempflax was used in the experiments. The used hemp material consisted of a large majority of core fibres (hemp hurds, which are a waste from hemp stem processing) prevailing over bast fibres and it also contained fine dust particles originating from a manufacturing crushing process. The original hemp hurds slices had a wide particle length distribution (8 to 0.063 mm). The mean particle length of the used hemp hurds was 1.94 mm. The density of the hemp material was 117.5 kg/m^3.

The content of polysaccharide component (holocellulose) of the used material is 77.3 %. The amounts of cellulose and hemicelluloses like holocellulose components are 44.5 and 32.8 %, respectively. Other components present in the hemp are lignin (22.0%), compounds soluble in toluene and ethanol (3.5 %), and ash (2.6 %).

Fig. 1 Hemp hurds

2.1 Hemp material treatment

Prior to treatment and in order to ensure constant moisture content, the fibres were dried at 80°C for 24h (to its constant weight) in a drying oven. The physical and physico-chemical modifications of the dried hemp hurds was realized by the ultrasonic treatment process (USG) for 1h. Distilled water and 0.2 M NaOH solution as cleaning medium were used in the experiments. In all cases of the surface treatment, the s:l (solid to liquid) ratio was 1:10. A TESON 10 ultrasonic bath (Tesla, Slovakia, 220 V, 50 Hz, power output of 650W) was used for the ultrasonic cleaning process of the hemp hurds. The hemp hurds samples were dried at 80°C to constant weight after all treatment steps.

2.2 Investigation methods

The FTIR measurements were carried out on a Bruker Alpha Platinum spectrometer using the Attenuated Total Reflectance (ATR) technique (BRUKER OPTICS, Germany). Total 24 scans were performed on each sample in the range of 400-4000 cm-1. FTIR spectroscopy is capable of defecting structural changes in biomaterial. It provides the information about the presence or absence of specific functional groups or the formation of new functional groups, and can give an even deeper insight into the fibres structure. FTIR allows the identification of the main components of cellulose.

Scanning electron microscopy (SEM) observations of the hemp hurds were done on TESCAN MIRA 3 FE (TESCAN, Brno, Czech Republic). The fibre samples were glued on carbon adhesive films and coated with a carbon film using a vacuum sputtering coater. The samples were coated with the carbon film to avoid charging under the electron beam.

3 RESULTS AND DISCUSSION

The FTIR spectra for physico-chemically treated hemp hurds samples compared to the reference sample are shown in Figure 2. The main infrared spectral differences are observed, which allow identifying the structural changes in the lignocellulosic fibres after the physical and physico-chemical treatment. Peak positions corresponding to the vibrations of the functional groups present in the studied hemp hurds samples are consistent with the literature data published for vegetable fibres [12]. The range of wave number of 3570-2900 cm-1 is characteristic for the stretching vibrations of O-H and C-H bonds in polysaccharides. Based on paper [14], a broad band in the spectra range of 3490 - 3170 cm-1 represents the complex vibrations of hydroxyl stretching of inter- and intra-molecular hydrogen bonds. Its intensity decreases in the case of 0.2M NaOH treatment of the hemp hurds due to mercerization.

Many absorption bands corresponding to the vibrations of various functional groups present in the hemp components are observed in the region of 1800 to 900 cm-1. This range was employed to characterize the structure of hemicelluloses, lignin, but mainly of cellulose. The most visible differences in the spectra of the treated samples compared to the reference hemp hurds are presented and discussed only.

One such is the modification of the signal at 1733 cm-1, characteristic for the stretching vibration of an unconjugated C=O group in the acetyl groups in hemicelluloses [15]. This peak has partially disappeared after the treatment with NaOH in accordance with paper [16]. Indeed, NaOH treatment is known to remove hemicelluloses [17]. The peak at 1030 cm-1 belongs to the C-C, C-OH, C-H ring and side group vibrations in hemicelluloses and pectin.

Based on the observation of the sharp peaks located at 1507 cm-1 (C-C stretching from aromatic ring) in the FTIR spectra, ultrasonic treatment as well as the NaOH treatment led to a partial removal of lignin. The extraction of lignin was confirmed by the high-intensity ultrasonic treatment of the hemp fibres [18]. According to literature data [17], lignin cannot be totally removed by the alkaline process. As it is evident from Figure 2, the peaks typical for lignin were clearly observed at 1319 cm-1 in all samples.

Typical bands assigned to cellulose were observed at 896 cm-1 and in the region of 1630¬-1160 (Figure 2). The peaks at 1337 and 896 cm-1 represent O-H bending vibrations in cellulose. The band about 1320 cm-1 corresponds to -CH2- wagging vibration, which distinguished between amorphous and crystallised cellulose [19]. The hemicelluloses removal was confirmed by determining the chemical composition (Table 1) of hemp hurds particles as well as a partial removal of impurities and ash.

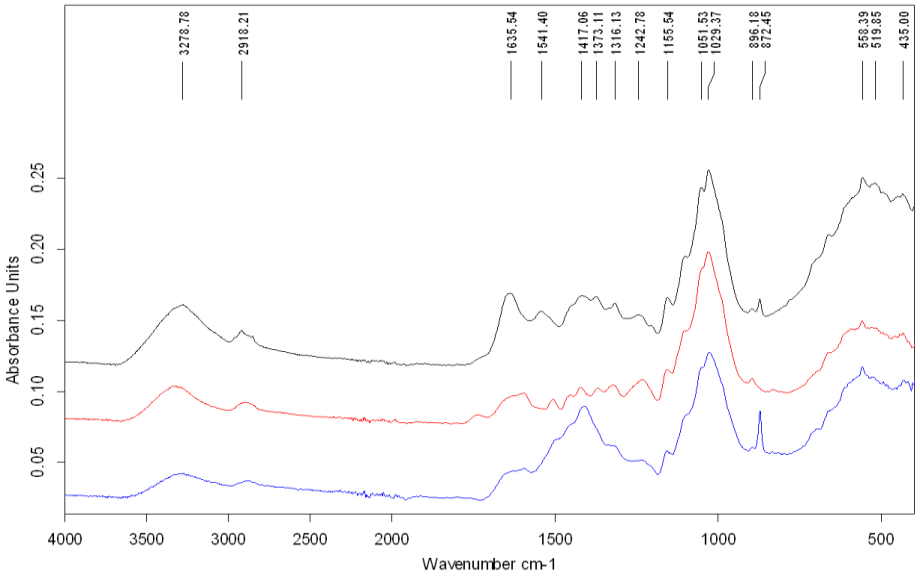

Fig. 2 FTIR spectra of hemp hurds: reference (black); ultrasonic treated (red); ultrasonic modified with 0.2M NaOH solution (blue)

Hemicelluloses removal was confirmed by determining the chemical composition (Table 1) of hemp hurds particles and also there is a partial removal of impurities and ash.

Tab. 1 Changes in chemical composition of hemp hurds before and after treatment

Main components of hemp hurds [%]	Reference	USG	USG 0.2M NaOH
Holocellulose	77.3	77.75	68.82
Cellulose	44.5	46.7	45.08
Hemicelluloses	32.8	32.6	23.74
Lignin	22.0	23.3	24.12
Compounds soluble in toluene and ethanol	3.5	2.6	4.15
Ash	2.6	1.3	1.91

The fibre quality was checked using Scanning Electron Microscopy (SEM) to reveal surface roughness, imperfections, and overall geometry. The examinations were carried out on original and treated hemp fibres to find out the morphological changes. The SEM micrographs of surface of lignocellulosic fibres from original hemp hurds (a), hemp hurds after ultrasonic treatment, and (b) ultrasonic treatment with NaOH (c) are shown in Figure 3. The hemp fibre surface topography showed the presence of surface impurities like ash and waxes. The fibre structure is formed by several bundles of filaments aligned by the plant´s length. The cleaning of surface after the treatments can be seen, and in addition, after the ultrasonic treatment with the 0.2M NaOH solution a partially fibrillate structure was observed as well.

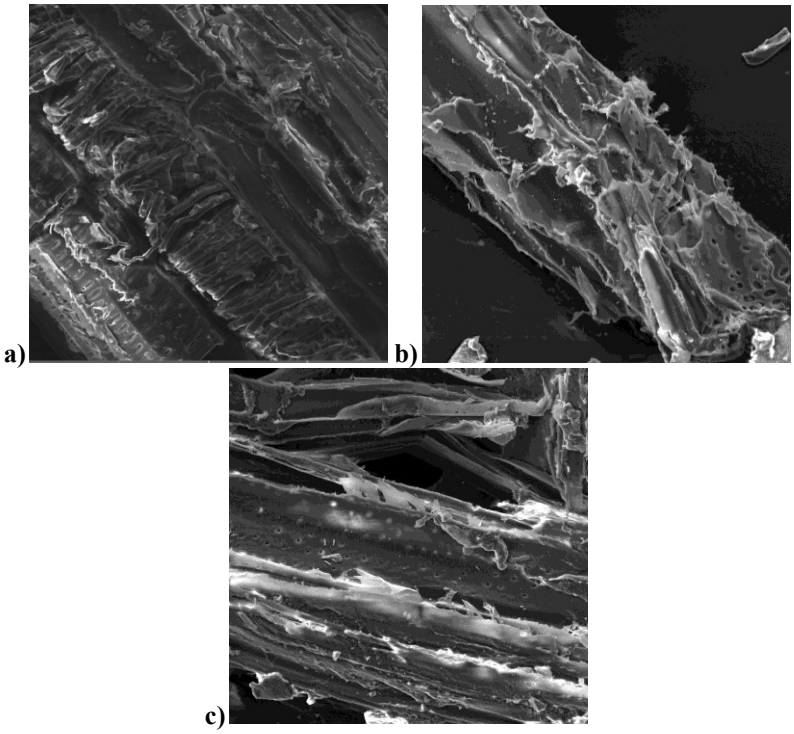

Fig. 3 SEM micrographs of hemp hurds samples: reference (a); ultrasonic (USG) treated (b); USG treated with 0.2M NaOH solution (c); (1500 times of magnification)

4 CONCLUSION

The present paper is devoted to FTIR and SEM investigations of hemp hurds changes caused by physical and physico-chemical treatments. The modification of the hemp hurds by the ultrasonic treatment was used as a method for the removal of organic and inorganic loosely bound contaminants from the hemp fibres surface in the experiments. As the FTIR spectroscopy shows, the non-cellulosic components, such as hemicelluloses, lignin, and waxes, after completing all treatment processes of the hemp hurds, were partially removed in dependence on the cleaning medium during the treatment procedure. These findings correspond with the changes in the chemical composition of the hemp material as well as with the SEM micrographs of the hemp hurds surface. The best result of degradation of these non-cellulosic materials was reached by the ultrasonic alkaline treatment in the 0.2 M NaOH solution.

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